



US Army Corps of Engineers



Testing Multi Increment[®] (MI) Soil Samples for Metals: To Grind or Not to Grind

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MI Approach: A Shakespearean Perspective

To grind, or not to grind: that is the question
Whether 'tis nobler in the mind to suffer
The slings and arrows of outrageous
variability,

Or to grind and take arms against a sea of
troubles from regulators and risk assessors...

To sleep: perchance to dream unground
samples are reproducible: ay there's the rub;
For in that reliance what decision errors may
come...





MI Lab Study for Metals

- Objective: Determine if good lab sub-sampling precision is possible if MI samples are not ground.
- Co-contributors:
 - ▶ Alan Hewitt, Cold Regions Research (CRREL) Engineering Lab, Hanover New Hampshire
 - ▶ Brian Jordan, Albuquerque District.
- MI samples from Site Investigation (SI) under Military Munitions Response Program (MRRP).



“Fort Sun Shine” Site Investigation

- SI Objective: Determine if lead (Pb) contamination from former pistol & rifle ranges exceeds 400 mg/kg in surface and subsurface soils at housing areas.
- 3 Munitions Response Sites (ranges) divided into 11 surface (0 - 1 ft) and 11 subsurface (1 - 2 ft) soil sampling units (SUs).
- 40-increment MI samples (≈ 1 kg) collected from each SU ($\approx 0.2 - 2$ acres).

Experimental Design of Lab Study

- 3 MI samples used for the sub-sampling study
 - ▶ P1 – Pistol Range (P) surface soil SU
 - ▶ P2 – Pistol Range (P) sub-surface soil SU
 - ▶ R3 – Rifle Range (R) surface soil SU
- Each sample sub-sampled using two methods
 - ▶ **Method A** – Method 8330B-like procedure
Sample spread on tray. 10-g sub-sample from 30-increments.
 - ▶ **Method B** – 8-chamber rotary splitter (500 increments per vessel). 15 10-g sub-samples.



Experimental Design

Number of Replicate Sub-samples

Sample	Method A	Method B
P1	15	15
P2	15	15
R3	15	15

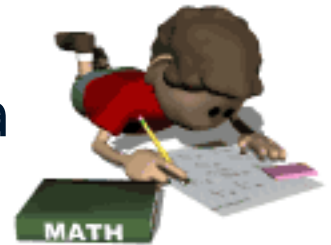


- Expected results:
 - Normal distributions & small Percent Relative Standard Deviations (%RSDs).
 - $\mu_A = \mu_B$ (equal means), $\sigma_A > \sigma_B$ (unequal std. deviations) (Method A uses 30 & Method B 500+ increments)

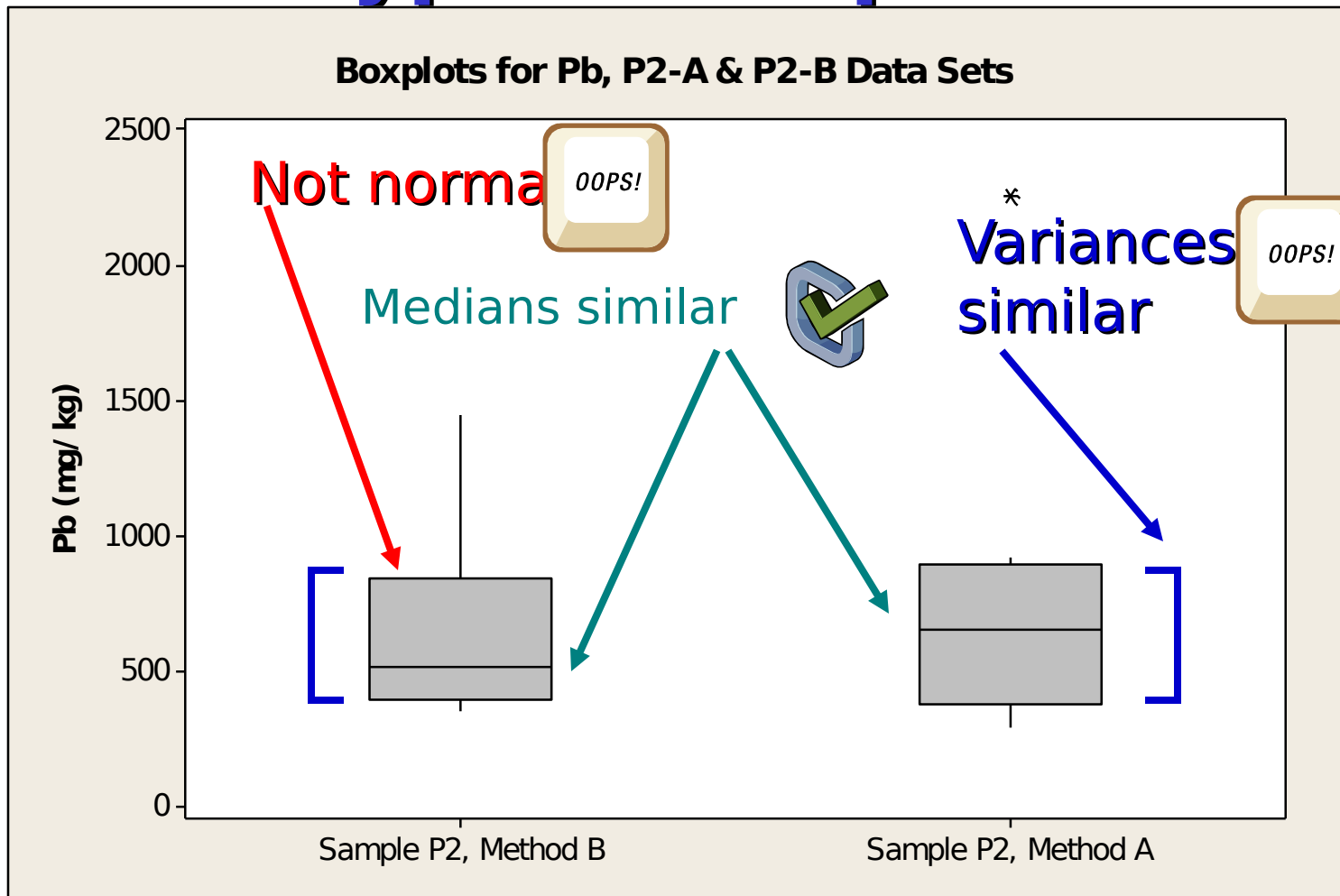


Top 5 Reasons to be a Statistician

1. You can safely comment on a colleague's lack of normality.
2. It is OK to be significantly different.
3. You can say you're correct 95% of the time.
4. You will never need to say that you're 100% certain.
5. You can have your head in a cooler and your feet in the fire but claim that on the average you're doing fine.



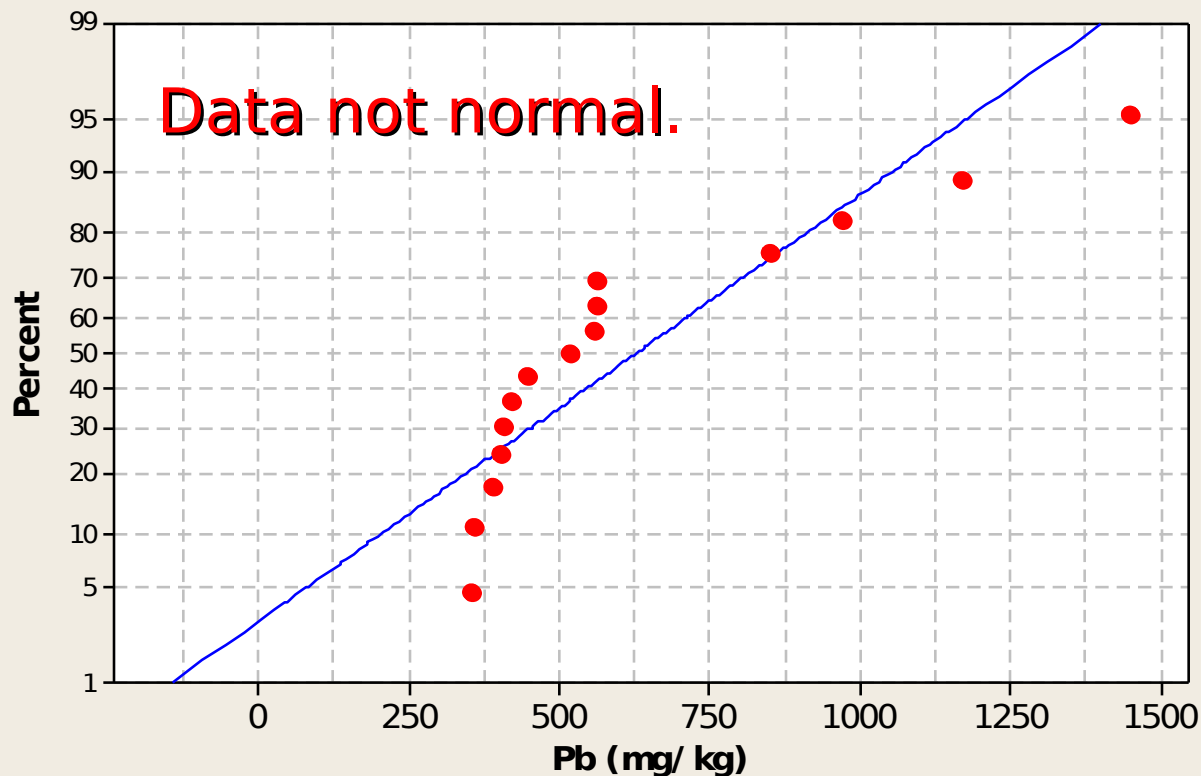
Typical Boxplot



Typical Normal Probability

Pb for Sample P2, Method B (% RSD = 53%)

Normal



Mean	627.8
StDev	331.7
N	15
Rj	0.886
P-Value	<0.010

$p = < 0.01$



Hypothesis Tests for Median

- Mann-Whitney Test (non-parametric test, Minitab)

Pb, Sample P2, Methods A and B

n Median, η (Eta), mg/kg

P2, Method B Pb 15 520.0

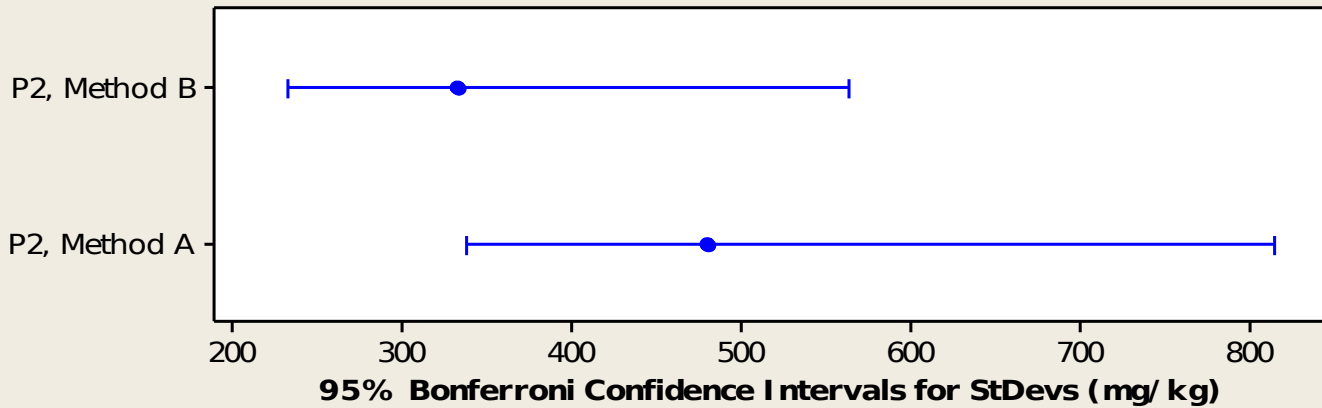
P2, Method A Pb 15 656.0

$H_0: \eta_A = \eta_B, H_1: \eta_A \neq \eta_B$

p-value = probability medians are equal = 0.62

p-value < 0.05 $\rightarrow$ 95% confidence that $\eta_A \neq \eta_B$

Test for Equal Variances for Pb, Sample P2, Methods A & B

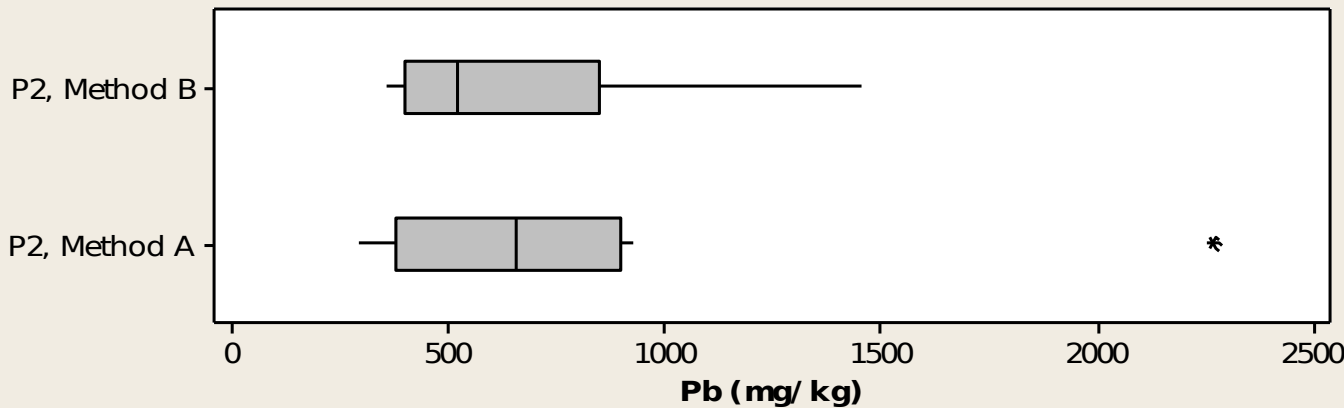


F-Test	
Test Statistic	0.48
P-Value	0.180
Levene's Test	
Test Statistic	0.41
P-Value	0.526

$$p = 0.53$$

$$H_0: \sigma_A = \sigma_B$$

$$H_1: \sigma_A \neq \sigma_B$$





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Metals	Methods A & B	Levene's Test (Variances)	Mann- Whitney (Medians)
Pb	P1	0.374	0.481
	P2	0.526	0.619
	R3	0.120	0.868
Cu	P1	0.973	0.803
	P2	0.953	0.135
	R3	0.130	0.604
Zn	P1	0.127	0.229
	P2	0.223	0.520
	R3	0.064	0.772

**p >
0.05**

Why did Method B (rotary splitter) give same variance as Method A?

- Flaw in experiment design.
- Lab blended samples with rotary splitter (Method B) prior to taking 30 increment sub-sample (Method A) ! Statistical tests were comparing soils that both passed through the same rotary splitter.
- Results still usable for evaluating precision for rotary splitter.



Evaluation of Precision

$$\%RSD = (s / \bar{x}) \times 100 \approx \text{Fundamental Error (FE)}$$

$$FE = 100 (22.5 \times d^3/M)^{1/2}$$

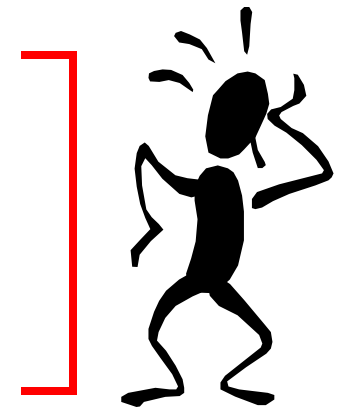
d = Maximum particle size (0.2 cm)

M = Mass of sub-sample (10 g)

$$FE = 13\%$$

%RSD >> FE = 13%

Sample	Method	Mean Pb (mg/kg)	Std. Pb (mg/kg)	%RSD (<i>n</i> = 15)
P1	A	540	670	120%
	B	770	730	95%
P2	A	730	480	66%
	B	630	330	53%
R3	A	12	1.7	14%
	B	12	1.1	9.2%



Data usually not normal if %RSD > 20% – 30%.

Why didn't rotary splitter result in good lab sub-sampling precision?



- $FE \neq 100$ ($22.5 \times d^3/M$)^{1/2} if samples contain nuggets (pure particles of contaminant).
Samples P1 and P2 contained nuggets of Pb.
- Conc. (mg/kg) of Pb from 1 – 2 mm particle in 10 g
 $M_{Pb} = V \times \rho = (4/3 \pi r^3) \times \rho$ (spherical particles)
 $r = 0.05 \text{ cm} - 0.1 \text{ cm}, \quad \rho = 11.34 \text{ g/cm}^3$ (density of Pb)
 $C = (6 - 48 \text{ mg})/0.010 \text{ kg} = \mathbf{600 - 4,800 \text{ mg/kg}}$
Pb conc. in sub-samples: **300 - 3000 mg/kg**



Conclusions



- Use an MI method for soils that contain metal particles (nuggets), as grab samples should result in very large variability.
- Rotary splitter can give good precision if soils don't contain nuggets; otherwise, large %RSDs (e.g., $\approx 100\%$) will be observed.
- To obtain good precision for soils with nuggets the particle size must be reduced (e.g., via grinding) or a large subsample mass must be analyzed (> 10 g).